Polysulfone and poly(phenylene sulfide) blends: 3. Rubber toughening

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Melt-blended polysulfone (PSF) and poly(phenylene sulfide) (PPS) are notch sensitive. A significant improvement in the notched Izod impact toughness occurs when at least 10 wt% of a shell-core rubber modifier is incorporated into the blend. At rubber modifier levels above 15 wt%, the notched Izod impact strength was essentially retained upon annealing at 160°C for 2 h, while below 15 wt% of rubber modifier, the notched Izod impact strength decreases after annealing under the same conditions. Izod impact fracture surface morphology was studied using scanning electron microscopy (SEM). Fracture surfaces without a rubber modifier exhibit cavitation around the dispersed phase, i.e. PPS. On the other hand, fracture surface morphology of the rubber toughened blends with the same PSF/PPS composition show no cavitation surrounding the dispersed phase. Blend morphology was also studied using transmission electron microscopy (TEM).

(Keywords: polysulfone; poly(phenylene sulfide); blends)

INTRODUCTION

Polysulfone (PSF) and poly(phenylene sulfide) (PPS) form phase-separated blends at all compositions when solution or melt-blended[1,2]. Polysulfone is an amorphous polymer while poly(phenylene sulfide) is semicrystalline; the addition of PPS to PSF reduces the melt viscosity and improves the processibility of the blend system. Post-annealing of injection-moulded specimens was found to further increase the degree of crystallinity of the PPS[2]. In a previous paper[3], we reported that the mechanical properties of the PSF/PPS blends, such as flexural strength, flexural modulus, tensile strength and modulus, were found to increase after annealing at 160°C, which is 25°C below the glass transition temperature (T_g) of PSF, but is 75°C above the T_g of PPS. The heat deflection temperature (HDT) of the blends was also found to increase as a result of the annealing process. The tensile properties followed the simple rule of addition when the PPS content was below about 50 wt%. At higher PPS contents, the tensile strength was below the value expected from the addition rule, probably due to the outgassing of PPS at high temperature that resulted in molecular weight degradation of PSF[3] and interfacial debonding of the two phases[4]. It has been revealed by dynamic mechanical thermal analysis[2] that a small portion of the PPS in the presence of PSF remains amorphous at lower PPS concentrations, even after annealing. Also, at lower PPS contents, the blends exhibit a certain degree of ductility, as revealed by the tensile test[3]. The PSF/PPS blend systems, however, exhibit no gain in notched Izod impact toughness over the neat components, with the notched Izod impact strength of the blends, as reported previously[3], ranging from 27 to 56 J m^{-1}.

Thermoplastic elastomers used as impact modifiers are well known, and many systems have been reported in the literature[5], with probably the most well studied system being rubber toughened polystyrene. The impact modifier can be incorporated into the polystyrene matrix by mechanical blending[6], or by polymerizing the styrene monomer in the presence of dissolved rubber[7]. Rubber toughened nylon has also been extensively studied[8–11]. A number of reports, on the toughening of poly(vinyl chloride), have incorporated shell-core methacrylate–butadiene–styrene (MBS) type modifiers[12,13]. Fowler *et al.*[14] also reported a synergistic effect by using MBS and styrene–butadiene–styrene block copolymer rubber modifiers. In addition the improvement of the notched impact strength of PSF using a special block copolymer was reported by Noshay *et al.*[15].

We have found that the MBS impact modifier manufactured by the Rohm and Haas Company significantly improves the Izod impact strength of the PSF/PPS blends. In this present study, notched Izod impact testing was used to differentiate the effectiveness of rubber additives and scanning electron microscopy (SEM) was used to study the morphology of the fracture surface, with transmission electron microscopy (TEM) being employed to study the blend morphology.

EXPERIMENTAL

The MBS impact modifier, Paraloid EXL 3607, was provided by the Rohm and Haas Company, Stereon 840A, a butadiene–styrene multiblock copolymer, was

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obtained from the Firestone Synthetic Rubber and Latex Company, and Kraton D1101, a styrene–butadiene–styrene block copolymer, was from the Shell Chemical Company. All other raw materials that were used in this work were described in detail in the first paper of this series[2]. Unless otherwise specified, the PSF/PPS ratio was fixed at 70/30 by weight, with the rubber modifier content being varied. Blend preparation was carried out in a Haake single screw extruder model 254. All raw materials were pre-dried at 110°C for 16 h and then dry-blended prior to extrusion and subsequent injection moulding, as described previously[2]. The maximum temperature at the extruder was set at 280°C, and the mould temperature was set at 60°C throughout these experiments. Notched Izod impact test measurements and HDT determinations were carried out as described in the previous papers in this series[2,3].

The morphology of the notched Izod impact test fracture surfaces of the blends was examined with a Jeol 840A scanning electron microscope, operating at a 20 keV accelerating voltage; micrographs were obtained using the secondary electron imaging (SEI) mode. All of the fracture surfaces observed by scanning electron microscopy (SEM) had been previously coated with a thin conducting layer of carbon to prevent 'specimen-charging' by the electron beam. TEM specimens were prepared for observation by using procedures described in a previous paper[2]. Due to low contrast of the rubber-modifier phase, microtomed thin sections of the specimens were treated with OsO_4 vapour.

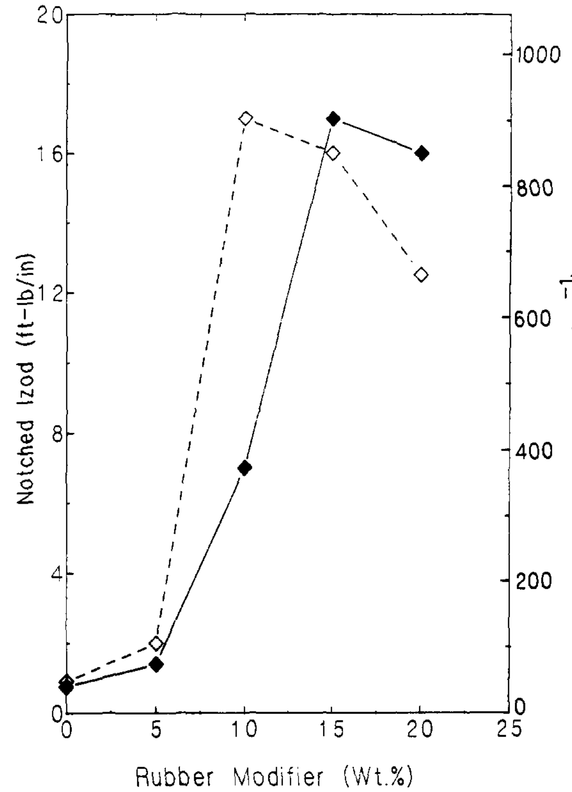

Figure 1 The variation of the notched Izod impact strength of a PSF/PPS (70/30) base blend as a function of the amount of added MBS rubber modifier: (◇) as-moulded; and (◆) annealed samples

RESULTS AND DISCUSSION

The addition of a rubbery additive to enhance the impact toughness of polymers is a common practice. Initially, several commercially available impact modifiers were investigated in order to determine the most effective one for these PSF/PPS blends, including additives such as styrene–butadiene block copolymers (e.g. Shell Chemical Company's Kraton or Firestone's Stereon), hydrogenated styrene–butadiene block copolymers (from the Shell Chemical Company) and a shell-core methacrylate–butadiene–styrene (MBS) impact modifier (such as Paraloid, from Rohm and Haas). The influence of these impact modifiers, at a level of 10 wt%, on the notched Izod impact strength of a PSF/PPS blend is shown in *Table 1*. The initial screening tests showed large differences in the impact strength data. Kraton and Stereon, known to be effective impact modifiers in various polymers, did not improve the notched Izod impact strength of the PSF/PPS blend, which reinforces the notion that the effectiveness of an impact modifier is matrix specific. Fowler and co-workers, for example, have reported that styrene–butadiene–styrene (SBS) particles toughened polystyrene but did not improve the properties of poly(methyl methacrylate) or styrene–acrylonitrile copolymers[14].

Table 1 The effect of various impact modifiers on the notched Izod impact strength of a PSF/PPS blend[a]

Modifier	Impact strength (J m^{-1})
Kraton D1101[b]	58.41
Stereon 840A[c]	79.65
Paraloid EXL 3607[d]	908

[a] PSF/PPS/impact modifier:72/18/10
[b] Styrene–butadiene–styrene block copolymer (Shell Chemical Company)
[c] Butadiene–styrene multiblock copolymer (Firestone Synthetic Rubber and Latex Company)
[d] Methacrylate–butadiene–styrene (MBS) copolymer (Rohm and Haas Company

The use of the shell-core impact modifier, Paraloid EXL 3607, was found to significantly improve the notched Izod impact strength of the PSF/PPS blend: the addition of 10 wt% rubber modifier brought about an increase in impact strength from about 50 to greater than 900 J m^{-1}. According to the manufacturer, this impact modifier has a shell-core structure of methacrylate–butadiene–styrene, comprising a hard shell and a rubbery core. With this kind of structure, the impact modifier can be dispersed relatively easily in the PSF matrix during compounding, as was indeed verified by microscopic studies of the morphology of the blends. The substantial improvement in impact properties is probably the result of improved dispersion, plus possibly a better interaction of MBS with the PSF matrix, when compared to the other impact modifiers tested in this study.

The influence of the concentration of the MBS rubber modifier on the notched Izod impact strength of a PSF/PPS (70/30) blend is shown in *Figure 1*, with both as-moulded and annealed results presented. The effects of annealing will be discussed later. The most interesting feature in *Figure 1* is an apparent optimum concentration of impact modifier, which seems to occur at around 10 wt%. At higher concentrations, e.g. 15–20 wt%, a gradual decrease in impact strength was observed. Although only a slight improvement in impact strength

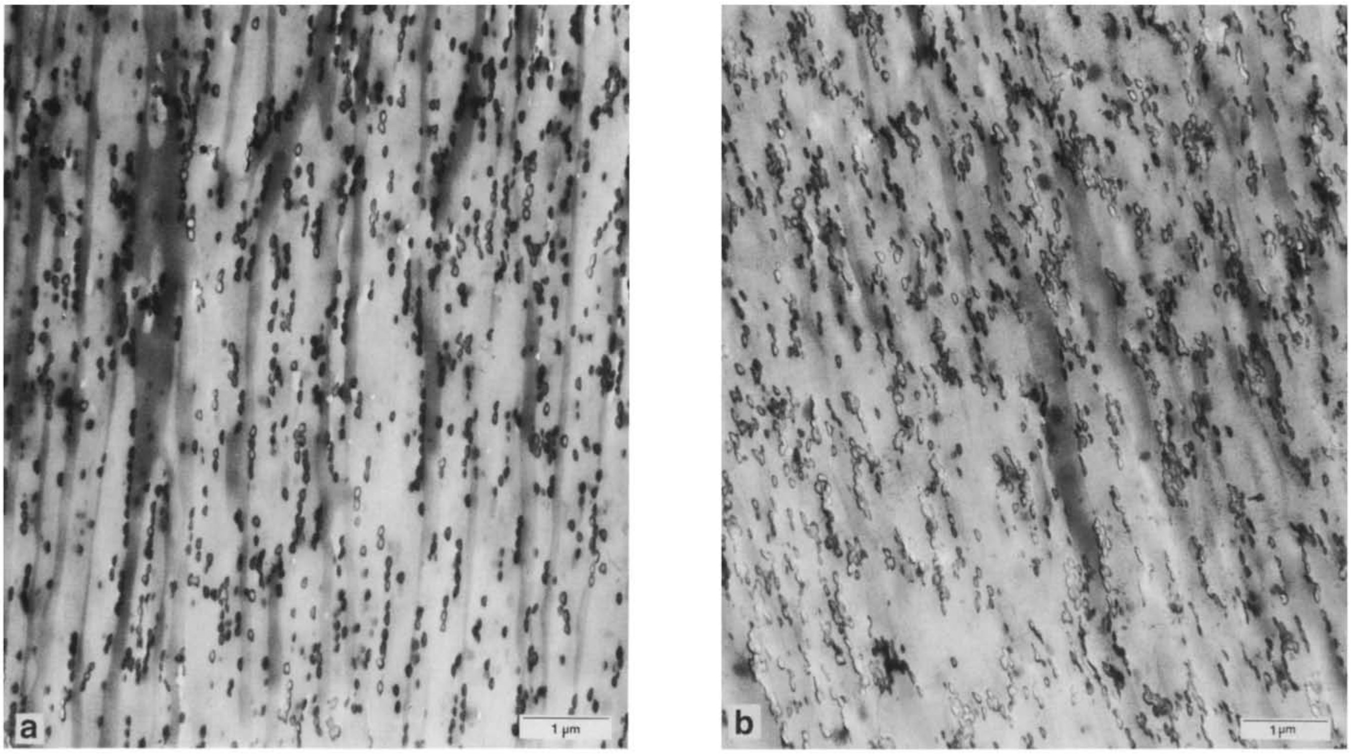

Figure 2 Transmission electron micrographs of a PSF/PPS (70/30) base blend containing: (a) 10 wt%; and (b) 15 wt% MBS rubber modifier

was seen at 5 wt% rubber content, preliminary results, using different compounding equipment, such as a reciprocating kneader extruder, have actually showed a large increase in impact strength at the 5 wt% level as well[16]. The fact that we observed an optimum concentration of impact modifier is believed to be related to the morphology of the blend, and the manner in which the MBS rubber is dispersed in it.

Typical transmission electron micrographs are shown in *Figures 2a* and *2b* for the PSF/PPS (70/30) blend, containing 10 and 15 wt% of impact modifier, respectively. The MBS rubber modifier is well dispersed into individual particles (the elongation along the flow direction is an artefact of microtomy), with the size estimated to be ~0.15 µm. Two distinct features can be identified on these micrographs. First, the discrete PPS phase (the darker phase) is more fibril-like and, secondly, the rubber modifier tends to segregate preferentially at or near the interface between the PSF matrix and the PPS dispersed phase. It is interesting to note that no rubber particles appear to be located in the PPS phase; in all cases, the rubber modifier resides in the PSF phase and at the interface. Moreover, when rubber particles are identified in the former, they are usually located very near to the interface. Increasing the modifier content to 15 and even 20 wt% did not result in either a better or a different dispersion of the rubber particles (as can be seen, for example, in *Figure 2b* for the case of 15 wt% rubber content). The rubber particles still segregate at or near the interface in what appears to be larger and more crowded agglomerations. Riess *et al.* have reported a similar phenomenon for other polymer blend systems[17]. They observed, for example, that a polyisoprene phase was located at the interface of a continuous poly(methyl methacrylate) phase and a dispersed polystyrene phase of that particular ternary blend system. These results suggest that, for PSF/PPS blends, the optimum level of impact modifier is a function of morphology, or size of the interfacial area. Since the morphology of PSF/PPS blends changes with composition[2], the optimum concentration of the MBS rubber modifier may also change.

Figure 3 shows the notched Izod impact results obtained for a series of blends with the MBS rubber modifier (Paraloid EXL 3607) content kept constant at 10% by weight while the ratio of PSF to PPS was varied. For comparison the impact strength data for PSF/PPS blends which contained no modifier are also shown; in this case the impact strength was found to be of the order of 50 J m^{-1} over the entire composition range. The MBS rubber was found to readily disperse in neat PSF, and the addition of 10 wt% resulted in more than a tenfold increase in impact strength to a value of ~800 J m^{-1}. On the other hand, dispersing the modifer in neat PPS proved difficult, and hence rubber modified PPS specimens were not moulded. The notched Izod impact strength of a PSF/PPS (80/20) blend with 10 wt% of MBS rubber is equivalent to that of the 10 wt% rubber modified, neat PSF system, and a slight increase is seen for the 70/30 and 65/35 PSF/PPS blends. This implies that the toughening effect is predominantly associated with the PSF phase, as corroborated by the TEM micrographs (see *Figure 2*). As discussed above, the slight increase in impact strength at 30 and 35 wt% PPS is possibly due to morphological variations[2], with most likely an increase in interfacial surface area accompanied by better distribution of the impact modifier at and near the interface. As the content of PPS in the PSF/PPS blends increases, the PPS domains also increase and, when the amount is above about 50 wt%, the morphology changes from a PSF- to a PPS-continuous phase, as described in detail elsewhere[2]. Since the PPS phase is

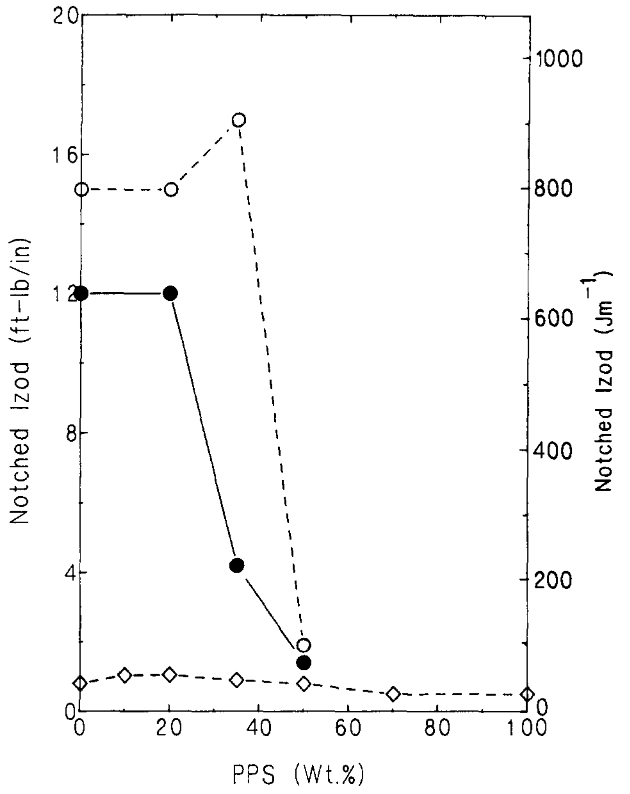

Figure 3 The variation of the notched Izod impact strength as a function of the composition of a series of PSF/PPS blends containing a constant amount (10 wt%) of MBS rubber modifier: (○) as-moulded; (●) annealed; and (◇) without modifier

not 'toughenable' by the MBS rubber, the impact strength would be expected to decrease when PPS is above a certain concentration, as is indeed the case at 50 wt% PPS.

The properties of annealed blends are of interest since in some applications the material may be exposed to elevated temperatures, e.g. in automotive engine components. Also, if the components are to be painted, the blends may undergo rapid changes during paint baking since paint-oven temperatures are usually above the T_g of the material. In the case of annealing PSF/PPS blends at 160°C, the major change was found to be an increase in PPS ($T_g = 85°C$) crystallinity[2], with the crystallization accompanied by a volume reduction of the PPS phase and an increased brittleness. The contraction, ageing, and embrittlement of amorphous PSF ($T_g = 185°C$) during annealing at 160°C are much slower, because its T_g is significantly higher than the annealing temperature. As a result of the difference in the contraction rates of PSF and PPS, it is possible that annealing would result in increased stresses at the interface, as well as some delamination.

Annealing was found to bring about a decrease in impact strength, the extent of which depended on the blend composition, the impact modifier concentration, and the annealing conditions. In the case of neat PSF containing 10 wt% rubber modifier, annealing at 160°C for 2 h resulted in about a 20% drop in impact strength (see *Figure 3*). A similar decrease was also seen in the PSF/PPS (80/20) blends which contained 10 wt% rubber modifier. At higher levels of PPS content, however, e.g. 35 wt% PPS, the impact strength decreased by about 75% after annealing, as seen in *Figure 3*. Thus, the PSF/PPS blends appear to be less 'toughenable' with higher levels of PPS. When the concentration of the impact modifier is 15 wt% or higher, annealing did not result in a decrease in impact strength (see *Figure 1*). In fact, at 20 wt% rubber content, a slight improvement was observed. We have no explanation for this observation, except to suggest that, possibly, the impact modifier 'eased' the interfacial stresses, due to its low modulus. In addition, because the impact modifier was found to be mostly at, or near the interface, it perhaps acted as a compatibilizer for this immiscible blend.

Figures 4 and *5* show, respectively, the influence of annealing temperature and annealing time on the impact properties of the rubber toughened blends. The influence of annealing for 2 h at various temperatures on the notched Izod impact strength (*Figure 4*) showed about 50% reduction in the impact strength at and above 160°C for the PSF/PPS (70/30) blend which contained 10 wt% rubber modifier. At lower test temperatures there was little change in the impact strength upon annealing. In

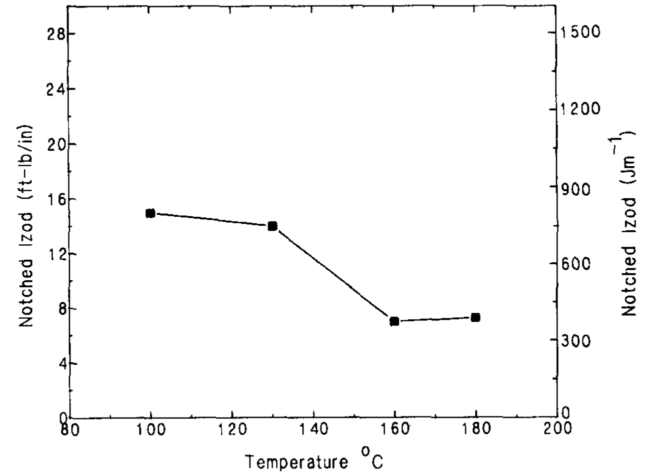

Figure 4 The variation of the notched Izod impact strength as a function of temperature for a PSF/PPS (70/30) base blend containing 10 wt% of MBS rubber modifier, which had been annealed for 2 h

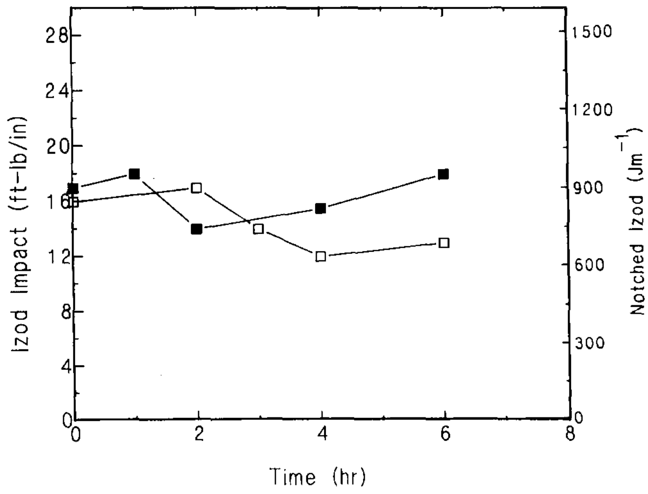

Figure 5 The variation of the nothced Izod impact strength as a function of annealing time of a PSF/PPS (70/30) base blend for the systems: (■) containing 10 wt% of MBS rubber modifier, after annealing at 130°C; and (□) containing 15 wt% of MBS rubber modifier, after annealing at 160°C

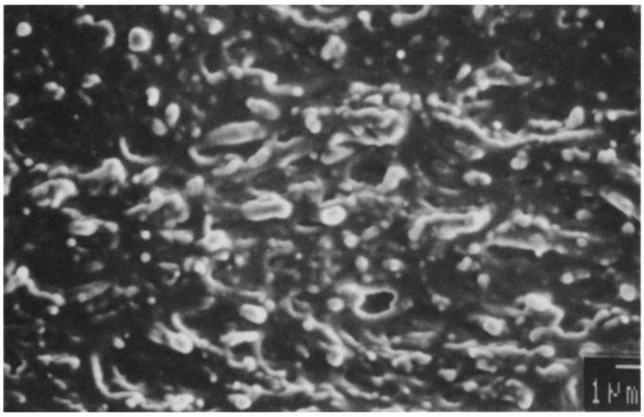

Figure 6 Scanning electron micrograph of the Izod impact fracture surface of an as-moulded PPS/PSF (20/80) blend

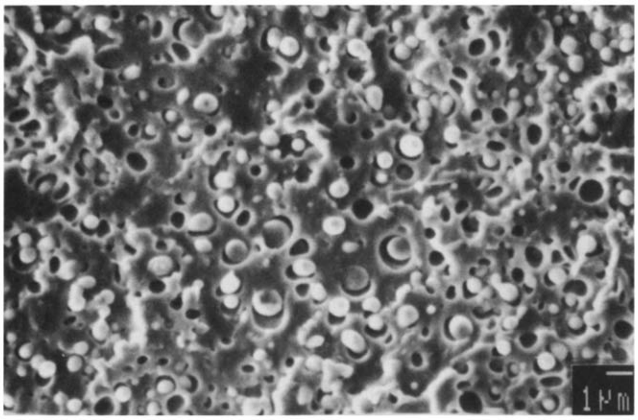

Figure 7 Scanning electron micrograph of the Izod impact fracture surface of an as-moulded PPS/PSF (20/80) base blend containing 10 wt% MBS rubber modifier

fact, after 6 h at 130°C, the PSF/PPS (70/30) blend with 10 wt% rubber modifier showed essentially no change in the impact strength (*Figure 5*). To counteract the effect of annealing at temperatures of 160°C, or higher, additional impact modifier may be added. Thus, with 15 wt% rubber modifier, about 20% decrease in impact strength was seen after 6 h at 160°C (*Figure 5*).

As reported previously[3], SEM investigations of the Izod impact fracture surface morphology of a PSF/PPS (80/20) blend, with no impact modifier, showed cavities around the dispersed PPS phase (see *Figure 6*). In contrast, *Figure 7* shows the fracture surface morphology of a 10 wt% rubber toughened PSF/PPS (80/20) blend, where no cavitation is observed. As suggested above, this may be due to the rubber's ability to relieve interfacial stresses and its compatibilizing effect.

CONCLUSIONS

The use of various rubber toughening additives in PSF/PPS blends was investigated and it was found that a shell-core methacrylate–butadiene–styrene impact modifier was the most effective in such systems. Other impact modifiers, such as butadiene–styrene copolymers or block copolymers, do not improve the Izod impact toughness of these blends. With up to 15 wt% rubber toughening additive in a PSF/PPS (70/30) base blend, the notched Izod impact strength increases from 53 to 849 J m^{-1}. More importantly, the impact strength at this rubber modifier content, after annealing at 160°C for 2 h, essentially does not change, and even the presence of PPS, a semicrystalline polymer which becomes brittle after crystallization takes place, does not seem to affect the toughness. We have found this post-anneal toughness to be a valuable property, as post-processing is usually an important, and sometimes a necessary, step in the fabrication of plastic components. Scanning electron micrographs of the impact fracture surfaces reveal that there are no cavities surrounding the dispersed PPS phase of the rubber toughened specimen, while transmission electron micrographs showed that rubber additives tend to accumulate between the matrix and the dispersed phases. This latter feature may play an important role in the toughening process and help absorb the stress from the interface during the Izod impact testing.

REFERENCES

1 Zeng, H. and Mai, K. *Makromol. Chem.* 1986, **187**, 1787
2 Cheung, M.-F., Golovoy, A., Plummer Jr, H. K. and van Oene, H. *Polymer* 1990, **31**, 2299
3 Cheung, M.-F., Golovoy, A. and van Oene, H. *Polymer* 1990, **31**, 2307
4 Cheung, M.-F. and Plummer Jr, H. K. *Polym. Bull.* 1991, **26**, 349
5 Bucknall, C. B. 'Toughened Plastics', Applied Science, London, 1977
6 Angier, D. J. and Fettes, E. M. *Rubber Chem. Technol.* 1965, **38**, 1164
7 Amos, J. L. *Polym. Eng. Sci.* 1974, **14**, 1
8 Flexman, E. A. *Polym. Eng. Sci.* 1979, **19**, 564
9 Hobbs, S. Y., Bopp, R. C. and Watkins, V. H. *Polym. Eng. Sci.* 1983, **23**, 380
10 Wu, S. *Polymer* 1985, **26**, 1855
11 Borggreve, R. J. M., Gaymans, R. J. and Eicheuwald, H. M. *Polymer* 1989, **30**, 78
12 Petrich, R. P. *Polym. Eng. Sci.* 1973, **13**, 248
13 Breuer, H., Haaf, F. and Stabenow, J. *J. Macromol. Sci. Phys.* 1977, **14**, 387
14 Fowler, M. E., Keskkula, H. and Paul, D. R. *Polymer* 1987, **28**, 1703
15 Noshay, A., Matzner, M., Barth, B. P. and Walton, R. K. *Adv. Chem. Ser.* 1976, **154**, 302
16 Golovoy, A., Cheung, M.-F., Plummer Jr, H. K., Paputa Peck, M. C. and Bauer, D. R. *SPE-ANTEC* 1993, 2686
17 Riess, G., Schlienger, M. and Marti, S. *J. Macromol. Sci. Phys.* 1980, **17**, 355